COMPLEX ORGANICS IN LABORATORY SIMULATIONS OF INTERSTELLAR/COMETARY ICES

M. P. Bernstein, L. J. Allamandola and S. A. Sandford

NASA-Ames Research Center, MS 245-6, Moffett Field CA 94035-1000, U.S.A.

ABSTRACT

We present the photochemical and thermal evolution of both non-polar and polar ices representative of interstellar and pre-cometary grains. Ultraviolet photolysis of the *non-polar* ices comprised of O_2, N_2, and CO produces CO_2, N_2O, O_3, CO_3, HCO, H_2CO, and possibly NO and NO_2. When *polar* ice analogs (comprised of H_2O, CH_3OH, CO, and NH_3) are exposed to UV radiation, simple molecules are formed including: H_2, H_2CO, CO_2, CO, CH_4, and HCO· (the formyl radical). Warming produces moderately complex species such as CH_3CH_2OH (ethanol), $HC(=O)NH_2$ (formamide), $CH_3C(=O)NH_2$ (acetamide), R-CN and/or R-NC (nitriles and/or isonitriles). Several of these are already known to be in the interstellar medium, and their presence indicates the importance of grain processing. Infrared spectroscopy, ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, and gas chromatography-mass spectrometry demonstrate that after warming to room temperature what remains is an organic residue composed primarily of hexamethylenetetramine (HMT, $C_6H_{12}N_4$) and other complex organics including the amides above and polyoxymethylene (POM) and its derivatives. The formation of these organic species from simple starting mixtures under conditions germane to astrochemistry may have important implications for the organic chemistry of interstellar ice grains, comets and the origins of life. © 1997 COSPAR. Published by Elsevier Science Ltd.

INTRODUCTION

Understanding the chemical and physical history of matter in the dense interstellar medium (ISM) is important since it is these materials that are the ultimate building blocks of new stars, planetary systems, and life. Our Solar System formed only some 4.55 billion years ago in a Universe perhaps 15 billion years of age, so it is clear that most interstellar materials have a long and complex history before ever becoming part of a solar system. Understanding the extraterrestrial evolution of chemical complexity is crucial to understanding both the early chemical state of our own solar system and the frequency with which similar or related conditions exist elsewhere in the universe.

During the past two decades ground, air, and space-based infrared astronomy, combined with realistic laboratory simulations, have revolutionized our understanding of interstellar ice and dust. Most interstellar material is concentrated in large molecular clouds where simple molecules are formed by gas-grain and gas phase reactions. Gaseous species striking the cold (10 K) dust will stick, forming an icy grain mantle (Sandford and Allamandola 1993).

The composition of interstellar ices is revealed by obtaining the infrared spectra of stars situated in or behind clouds. As the radiation from these infrared sources passes through the cloud, the intervening molecules absorb at their characteristic vibrational frequencies. The interstellar spectra and the spectra of with relevant materials prepared in the laboratory can then be compared directly in order to identify ice composition and determine molecular abundances (See Sandford 1996 for a recent review).

Gas phase species readily condense onto grains in dense molecular clouds forming ice mantles (Sandford and Allamandola 1993). Thus, interstellar ices should contain many of the same species seen in the gas phase (see van Dishoeck *et al.* 1993 for a review of identified interstellar gas phase species). Mantle compositions do not simply reflect gas phase abundances, however, since new compounds are formed

when reactive gaseous species condense on the grain surfaces and the ices are energetically processed by UV radiation and cosmic rays (cf. Tielens and Hagen 1982, d'Hendecourt *et al.* 1985, Allamandola *et al.* 1988, Brown and Charnley 1990, Hasegawa *et al.* 1992, Bernstein *et al.* 1995, Moore *et al.* 1996).

Since hydrogen is 3 to 4 of orders of magnitude more abundant than the next most abundant reactive heavier elements, grain surface chemistry is largely moderated by the local H/H_2 ratio. In regions where this ratio is large, H atom addition (hydrogenation) dominates and species such as CH_4, NH_3, and H_2O are expected to be prominent. If the H/H_2 ratio is substantially less than one, however, reactive species such as O and N are free to interact with one another forming molecules such as CO, CO_2, O_2 and N_2. Thus, two qualitatively different types of ice mantle may be produced by grain surface reactions, one dominated by polar, reduced molecules and the other dominated by non-polar, oxidized molecules.

Of course, the separation of molecules into nicely defined polar and non-polar ices is a gross over simplification. In reality, the composition and distribution of these two types of interstellar ices are likely to vary in a more graduated way and will depend on the history and current environment of the material. However, there is currently enough information to make some general conclusions about the relative distributions of these two classes of interstellar ice.

The evidence for the presence of ices dominated by non-polar components comes largely from the study of the CO (carbon monoxide) ice feature that falls near 2140 cm^{-1} (4.67 μm). The position, width, and profile of this feature are sensitive to the ice matrix in which the CO is frozen (Sandford *et al.* 1988). Many of the lines-of-sight that contain H_2O ice also contain CO ice and the relative strengths of the H_2O and CO bands indicate CO/H_2O ratios ranging from 0.0 to as much as 0.3. Although a few of the CO bands have positions and profiles consistent with much of the CO frozen in H_2O-rich matrices, *most* lines-of-sight exhibit profiles indicative of CO frozen in non-polar matrices, not H_2O (Sandford *et al.* 1988, Tielens *et al.* 1991, Chiar *et al.* 1995). Our recent laboratory studies of the CO feature indicate that these non-polar ices are most likely dominated by O_2, N_2 and CO_2 (Figure 1 from Elsila *et al.* 1997), the sorts of molecular
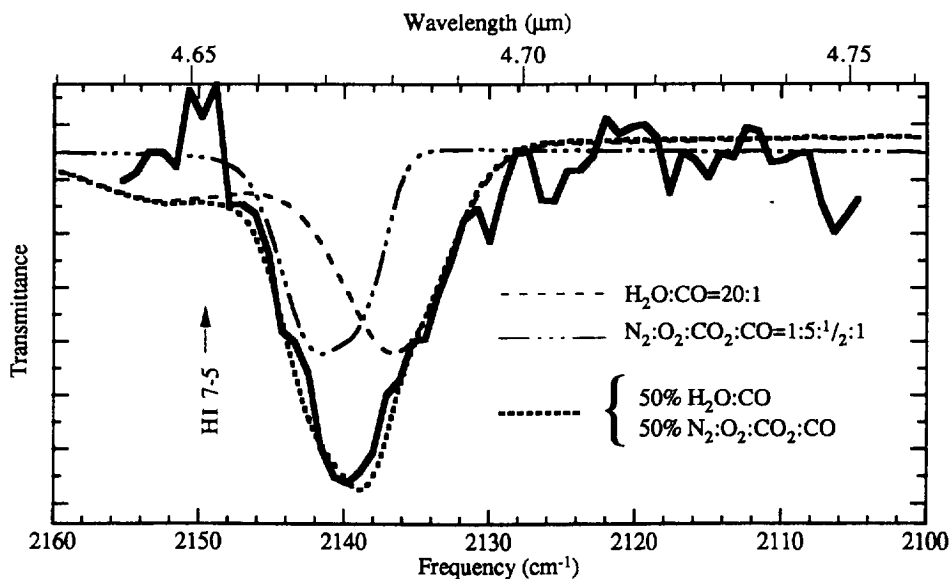

Fig 1. The 2160-2100 cm^{-1} (4.63-4.76 μm) infrared spectrum of Elias #18 (from Tielens *et al.* 1991) and fits to lab CO features implying the presence of a non-polar ice dominated by O_2 & N_2.

species that one would expect where $H/H_2 < 1$. Additional interstellar ice constituents consistent with this environment include CO_2 and OCS or CO_3. Let us now consider polar ices. Figure 2 shows a comparison

between the spectrum of W33A, a protostar deeply embedded within a molecular cloud (Capps *et al.* 1978) with the laboratory spectra of various interstellar ice analogs. Other than the strong silicate absorption near 1000 cm^{-1} (10 μm) (Willner *et al.*1982), and the weak absorption near 2880 cm^{-1} (3.47 μm), from micro diamonds (Allamandola *et al.* 1992), all other absorptions are caused by ices. Comparison of interstellar and laboratory spectra like those shown in Figure 2 have led to the characterization of polar ices dominated by H_2O and containing CO, CO_2, and CH_3OH (1-10% relative to H_2O), NH_3, H_2CO, (1-4%) and small amounts of CH_4, H_2, and more complex organic materials. A recent review on the composition of polar interstellar ices can be found in Sandford (1996).
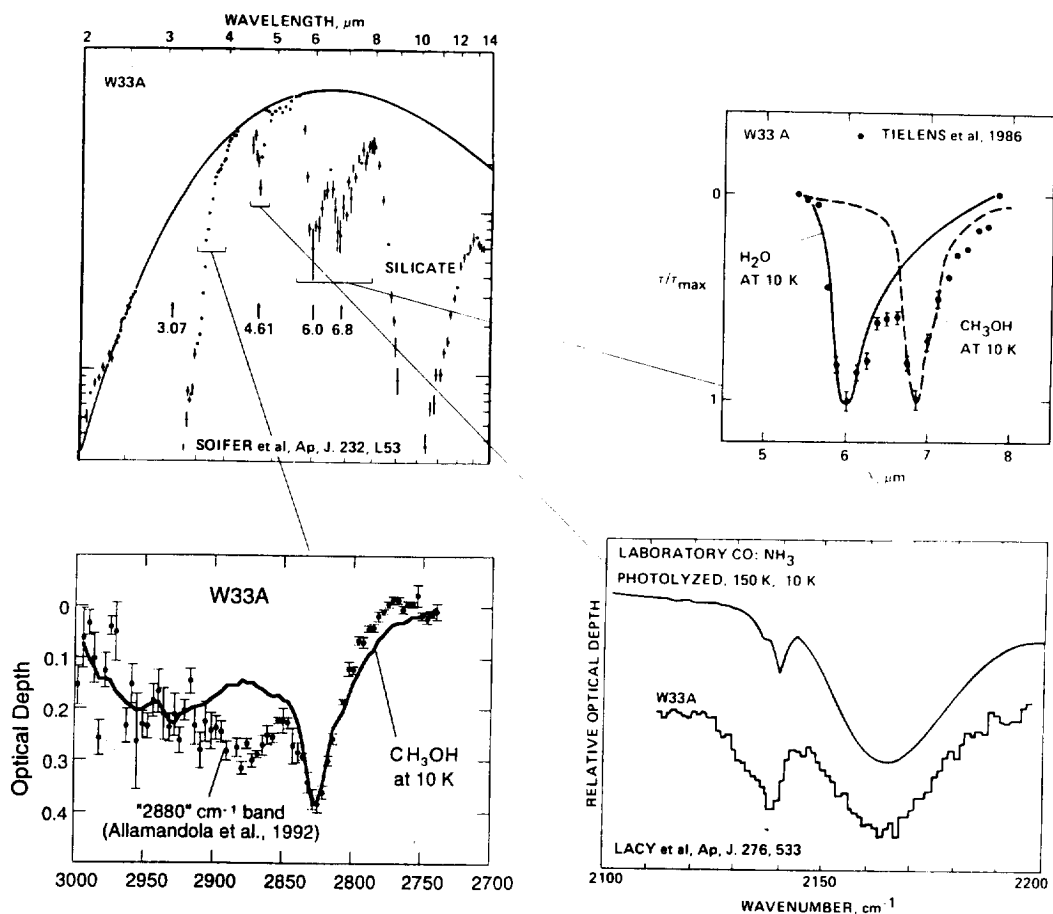

Fig 2. The spectra of laboratory analogs compared with that of W33A, a protostar deeply imbedded in a dense molecular cloud. Upper left - The interstellar spectrum of W33A represented by the points. Upper right - Comparison of W33A (points) with the lab spectra of H_2O (solid line) and CH_3OH (dashed line) ices. Lower left - Comparison of W33A (points) with the lab spectra of CH_3OH (solid line) in an H_2O-rich ice. Lower right - Comparison of W33A (lower heavy line) with a laboratory analog (upper narrow line). The absorption feature near 2140 cm^{-1} is CO and the broader feature centered near 2165 cm^{-1} is "XCN."

The fact that H_2O, a highly polar molecule, is the most abundant molecule in the ices along *all* lines-of-sight, but that the CO is mostly in *non*-polar ice provides clear evidence for the existence of multiple chemical environments along lines of sight where both are seen. Available data indicates that the polar ices are more common in lines of sight towards embedded protostars, while the non-polar ices tend to dominate towards field (background) stars (Elsila *et al.* 1997). This suggests that the non-polar ices are most abundant in the quiescent portions of dense clouds. The dearth of non-polar ices toward embedded protostars may be the result of ice sublimation in the warmer environments surrounding these objects, since ices dominated by N_2, O_2, CO_2, and CO will sublime at much lower temperatures leaving behind H_2O, CH_3OH, and NH_3 (Sandford and Allamandola 1993).

LAB STUDIES OF INTERSTELLAR ICE ANALOGS

We expect UV radiation to impinge on interstellar ices and this will modify or destroy some species, but create others. Any molecules formed in this manner may return to the gas phase and take part in other chemistry or become incorporated into forming solar systems. In any event we need to know the effect of radiation if we are to model ice mantles. Ices were formed by vapor deposition onto a CsI window at 12 K in a vacuum chamber at ~ 10^{-8} Torr. For further descriptions of the experimental set-up and procedures see Bernstein *et al.* 1995 and Elsila *et al.* 1997.

LAB STUDIES - NON-POLAR ICES

UV photolysis experiments of CO in mixtures containing various amounts of N_2, O_2, and CO_2 indicate that most of this photochemistry is driven by "hot" O atoms liberated by photolysis of O_2, or CO. The principle species produced from these O atom reactions are CO_2, N_2O, O_3, and CO_3. CO_2 is detected in all cases, and N_2O in most (Figure 3 from Elsila *et al.* 1997). Generally, as the concentration of CO decreases, N_2O production is favored over CO_2 production. Ozone appears as a photoproduct in all the mixtures, although the amount produced is highly variable. Relatively little O_3 is produced in N_2:CO and N_2:H_2O:CO ices while N_2:O_2:CO and N_2:O_2:CO_2:CO ices show the strongest ozone production. Photolysis of O_2-containing ices also produced carbon trioxide (CO_3). While there is some tentative evidence for the production of minor amounts of NO_2 and NO in these mixtures, the laboratory results indicate that few photoproducts containing a *single* nitrogen atom are formed, implying that N_2 is relatively immune to photolytic destruction under these conditions. For example, while "XCN" is easily made in the photolysis of *polar* interstellar ice analogs, (see below) it is *not* made when N_2-rich, non-polar ices are exposed to UV radiation.
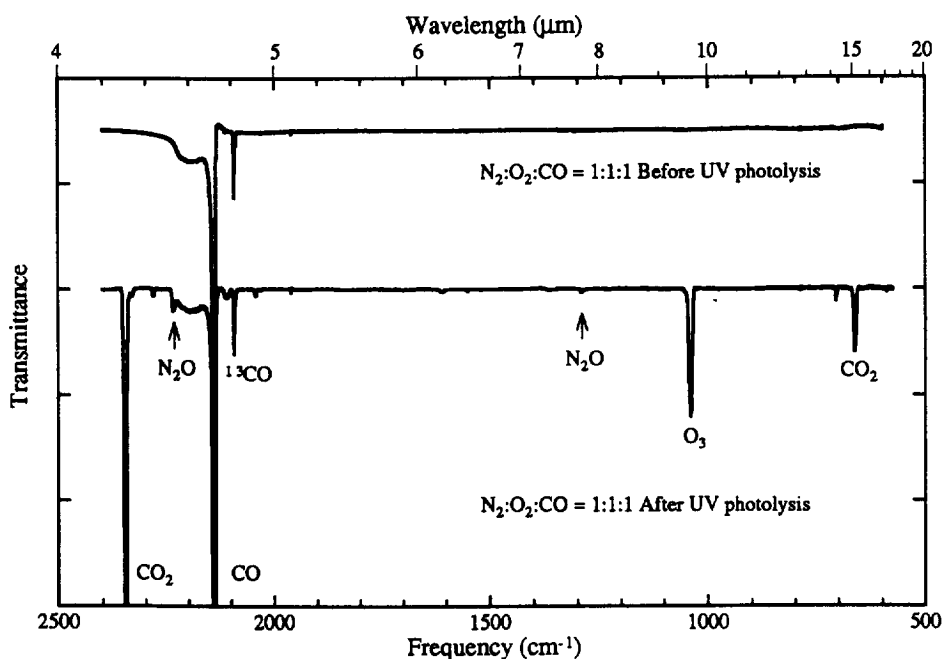

Fig 3. The 2500-500 cm^{-1} (4.0-20 μm) infrared spectrum of an N_2, O_2, CO mixture before and after UV photolysis at 12 K. The radiation is primarily Lyman α, but also contains continuum.

The UV irradiation of N_2-CO mixtures where small amounts of H_2O have been added, so the ice is non-polar in character, produce all of the same molecular species seen in the H_2O-free ices. In addition, the liberation of H from the H_2O produces the formyl radical, HCO·, and formaldehyde, H_2CO (Elsila *et al.*

1997). Since formaldehyde requires the addition of one more hydrogen atom than the formyl radical, it appears only when the H_2O concentration is high enough to be comparable to the other, non-polar components in the ice. Several other hydrogenated forms of CO and CO_2, such as HOCO, are also seen. The non-polar ices did not leave a noticeable organic residue at room temperature, in contrast to the polar ice analogs discussed below.

LAB STUDIES - POLAR ICES

Given the very different compositions of the polar and non-polar ices, it is not surprising that they yield very different photoproducts. The ultraviolet irradiation of polar ices dominated by H_2O and CH_3OH has far richer photochemistry than that described above. Infrared spectroscopy demonstrates that when polar ice analogs comprised of H_2O, CH_3OH, CO and NH_3 at 10 K (Figure 4a) are exposed to UV radiation this results in the destruction of methanol and the creation of several species (Figure 4b) including H_2CO (1720 & 1500 cm^{-1}), CO (2140 cm^{-1}), CO_2 (2340 & 665 cm^{-1}), and, not visible in this figure, H_2 (4140 cm^{-1}), CH_4,(3015 & 13-5 cm^{-1}) and HCO· (the formyl radical - 1870 & 1090 cm^{-1}), see Bernstein *et. al* 1995. Irradiated ices made from ^{13}C and D labeled starting materials (not shown) confirm that none of the photoproducts are the result of contamination and all but the formyl radical have been identified in interstellar ices, which implies that radiation processing is responsible for their production.
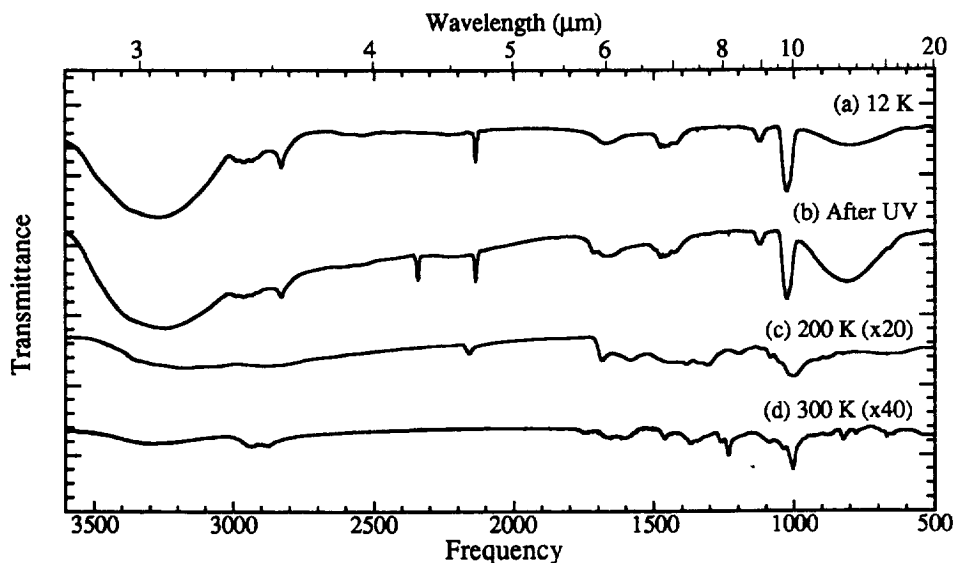

Fig 4. The 3600-500 cm^{-1} (2.78-20.0 μm) infrared spectra of: (a) a $H_2O:CH_3OH:CO:NH_3$ = 10:5:1:1 ice mixture at 12 K before UV photolysis, and the same ice mixture after (b) UV photolysis at 12 K for ~20 hours, (c) UV photolysis and warm up to 200 K, and (d) UV photolysis and warm up to 300 K. (Figure adapted from Bernstein *et al.* 1995).

With warming, the peaks corresponding to less stable species, such as H_2CO and the methyl and formyl radicals, vanish as they react, and the bands of volatile compounds such as H_2O, CO, CH_4, and CO_2 diminish as they evaporate. New peaks appear during warming as new bonds are formed by reactive species that become mobilized as the temperature increases. For example, at 200 K moderately complex species such as CH_3CH_2OH (ethanol), HC(=O)NH_2 (formamide), CH_3C(=O)NH_2 (acetamide), ketones, and nitriles including the "XCN" species (Figure 4c) are detected. Several of these are already known to be in the interstellar medium, and their presence indicates the importance of grain processing. (Many suggestions have been made as to the identity of "XCN" (Lacy *et al.* 1984, d'Hendecourt *et al.* 1986, Nuth & Moore 1988, and Grim and Greenberg 1987), but none have been embraced by the community)

After warming to room temperature an organic residue remains on the window (Figure 4d). Infrared spectroscopy, ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, and gas chromatography-mass spectrometry demonstrate that this organic residue is a mixture of non-volatile organic compounds comprised of hexamethylenetetramine (HMT, $C_6H_{12}N_4$), polyoxymethylene {POM, (-CH_2O-)$_n$} derivatives, amides, and ketones (Bernstein *et al.* 1995).

HMT formation depends on the presence of ammonia and formaldehyde which is, in these ices, a UV photoproduct of CH_3OH. Ices that do not contain methanol produce very little HMT (Agarwal *et al.* 1985, d'Hendecourt *et al.* 1986). Without UV radiation HMT *does not* form, even in ices of ammonia and formaldehyde, POM is made instead (Schutte, Allamandola, & Sandford 1993a,b). Perhaps UV radiation stimulates formation of the imine of formaldehyde, the first intermediate on the path to HMT.

$$H_2C=O + NH_3 \dashrightarrow H_2C=NH \text{ (imine of formaldehyde)} \dashrightarrow HMT$$

If the above equation applies to interstellar ice then one would certainly expect to see the imine of formaldehyde, and indeed it has recently been observed (Irvine 1996). For descriptions of the UV photolytic evolution of a variety of interstellar ice analogs, see Hagen *et al.* (1979), Agarwal *et al.* (1985), d'Hendecourt *et al.* (1986), Allamandola *et al.* (1988), and Bernstein *et al.* (1995).

IMPLICATIONS

"XCN", the putative nitrile or isonitrile mentioned above and seen near 2165 cm^{-1} in Figures 2 (lower right) and 4c is the strongest evidence of radiation processing within dense clouds (Lacy *et al.* 1984, Tegler *et al.* 1993). There is an indication that this feature is conspicuous in the spectra of embedded protostellar objects but not in that of background stars (Tegler *et al.* 1995). In laboratory experiments where the feature is made by the radiative processing of interstellar ices analogs, it is most prominent after warming (Bernstein *et al.* 1995) consistent with the notion that it is the heat from the protostar, acting on photo-processed ice that makes "XCN" obvious towards embedded objects. Although other nitriles are known to exist in the gas phase, (see Mann and Williams 1980; Irvine et al. 1987; van Dishoeck et al. 1993 for reviews) none have been measured in ice by infrared astronomy because telluric CO_2 blocks the relevant wavelengths. This may be changing thanks to ISO, and recent laboratory investigations of nitriles under planetary (Russo and Khanna 1996) and interstellar (Bernstein *et al.* 1997) conditions are in press.

Our detection of CH_3CH_2OH (ethanol), $HC(=O)NH_2$ (formamide), $CH_3C(=O)NH_2$ (acetamide), ketones {R-C(=O)-R'}, nitriles, HMT, and compounds related to POM in the photolysis residues of polar ices, as well as the identification of similar compounds in other ice analog experiments (Agarwal *et al.* 1985; Briggs *et al.* 1992; Schutte *et al.* 1993a,b) suggests that these species may be present in interstellar and cometary ices and thus have seeded the early Earth. In addition to the possible prebiotic activity of such molecules themselves, the products that derive from them should also be considered. For example, HMT photolysis produces nitriles and oxides of carbon, making it a good candidate for a common extended source of CN, H_2CO, and CO in the tail of comets (Bernstein *et al.* 1994). In addition HMT hydrolysis under acidic conditions yields ammonia, formaldehyde and amino acids (Wolman *et al.* 1971).

Finally, these organic residues from photolysis of interstellar ice analogs show lipid-like behavior when they are dissolved rapidly in water or methanol (Allamandola *et al.* 1997). The result is the formation of insoluble droplets, some of which selectively trap photoluminescent material from the residue. This behavior is reminiscent of simple membranes (Folsome 1979). All of these findings indicate that the organic material produced by the photolysis of ices in the interstellar medium may have had a profound effect on the formation of life in our solar system.

CONCLUSIONS

Infrared observations, combined with realistic laboratory simulations, have revolutionized our under-standing of interstellar ice and dust. Interstellar ices consist of both non-polar and polar components. The non-polar ices are dominated by species like O_2, N_2, CO, and CO_2 whereas polar ices contain H_2O,

CH_3OH, CO, CO_2, H_2, and probably some NH_3 and H_2CO. Based on laboratory studies of realistic ice analogs, we suggest that ultraviolet photolysis of the non-polar ices produces CO_2, N_2O, O_3, CO_3, HCO, H_2CO, and possibly NO and NO_2.

Photolysis of the polar, H_2O-rich ices yields H_2, H_2CO, CO_2, CO, CH_4, HCO, and warming reveals moderately complex organic molecules: CH_3CH_2OH (ethanol), $HC(=O)NH_2$ (formamide), $CH_3C(=O)NH_2$ (acetamide), "XCN" (nitriles), amides, ketones, HMT, and more complex molecules including polyoxymethylene and related species (POMs). The ultraviolet photolysis of HMT frozen in H_2O ice produces the "XCN" band observed in the spectra of protostellar objects and laboratory ices, as well as carbon oxides and other nitriles.

The ready formation of complex organic species from simple starting mixtures, under conditions germane to interstellar and cometary ices suggests that these materials may well be common in forming solar systems. The observation that the more complex refractory photoproducts show lipid-like behavior and readily form micelles upon exposure to liquid water suggest that the processing of interstellar ices may have played an important role in the origin of life.

REFERENCES

Agarwal, V.K., Schutte, W., Greenberg, J.M., Ferris, J.P., Briggs, R., Connor, S., Van De Bult, C.P.E.M., & Baas, F. (1985). Photochemical reactions in interstellar grains. Photolysis of CO, NH_3 and H_2O. *Origins of Life*, **16**, 21.

Allamandola, L.J., Sandford, S.A., & Valero, G. (1988). Photochemical and thermal evolution of interstellar/pre-cometary ice analogs. *Icarus* **76**, 225.

Allamandola, L.J., Sandford, S.A., Tielens, A.G.G.M., & Herbst, T.M. (1992). Infrared spectroscopy of dense clouds in the C-H stretch region: Methanol and "Diamonds". *ApJ* **399**, 134.

Allamandola, L.J., Bernstein, M.P., and Sandford, S.A. (1997). Photochemical evolution of interstellar/precometary organic material. In Astronomical and Biochemical Origins and the Search for Life in the Universe, C.B. Cosmocovici et al., Eds., Proc 5th Intl Conf. on Bioastronomy, IAU Coll. #161, Capri, 1-5 July 1996 in press.

Bernstein, M.P., Sandford, S.A., Allamandola, L.J., & Chang, S. (1994). Infrared Spectrum of Matrix-Isolated Hexamethylenetetramine in Ar and H_2O at Cryogenic Temperatures. *J Phys Chem* **98**, 12206.

Bernstein, M.P., Sandford, S.A., Allamandola, L.J., Chang, S., & Scharberg, M.A. (1995). Organic Compounds Produced by Photolysis of Realistic Interstellar and Cometary Ice Analogs Containing Methanol. *ApJ* **454**, 327.

Bernstein, M.P., Sandford, S.A., Allamandola, L.J.(1997). The Infrared Spectra of Nitriles and Related Compounds Frozen in Ar and H_2O. *ApJ In Press*

Briggs, R., Ertem, G., Ferris, J. P., Greenberg, J. M., McCain, P. J., Mendoza-Gomez, C. X., & Schutte, W. (1992). Comet Halley as an aggregate of interstellar dust and further evidence for the photochemical formation of organics in the interstellar medium. *Origins of Life and evolution of the Biosphere* **22**, 287-307.

Brown, P.D., & Charnley, S.B. (1990). Chemical models of interstellar gas-grain processes - I. Modelling and the effect of accretion on gas abundances and mantle composition in dense clouds. *MNRAS* **244**, 432

Capps, R.W., Gillett, F.C., & Knacke, R.F. (1978). Infrared observations of the OH source W33 A. *ApJ* **226**, 863.

Chiar, J.E., Adamson, A.J., Kerr, T.H., & Whittet, D.C.B. (1995). High resolution studies of solid CO in the Taurus dark cloud: Characterizing the ices in quiescent clouds. *ApJ* **455**, 234.

d'Hendecourt, L.B., Allamandola, L.J., & Greenberg, J.M. (1985). Time dependent chemistry in dense molecular clouds I. Grain surface reactions, gas/grain interactions and infrared spectroscopy. *A&A* **152**, 130.

d'Hendecourt, L.B., Allamandola, L.J., Grim, R.J.A., & Greenberg, J.M. (1986). Time dependent chemistry in dense molecular clouds II. Ultraviolet photoprocessing and infrared spectroscopy of grain mantles. *A&A* **158**, 119.

Elsila, J., Allamandola, L.J., and Sandford, S.A. (1997). The 2140 cm^{-1} Solid CO Band: The Case for Interstellar O_2 and N_2 and the Photochemistry of Non-Polar Interstellar Ice Analogs. *ApJ.*, in press.

Folsome, C.E., *The Origin of Life: A Warm Little Pond* (San Francisco: W.H. Freeman, 1979)

Grim, R. J. A., & Greenberg, J. M. (1987). Ions in grain mantles: The 4.62 micron absorption by OCN-in W33A. ApJ, **321**, L91.

Hagen, W., Allamandola, L.J., & Greenberg, J.M. (1979). Interstellar molecule formation in grain mantles: The laboratory analog experiments,results and implications. *Ap&SS* **65**, 215.

Hasegawa, T.I., Herbst, E., & Leung, C.M. (1992). Models of gas-grain chemistry in dense interstellar clouds with complex organic molecules. *ApJSS* **82**, 167.

Irvine, W. M., Goldsmith, P. F., & Hjalmarson, Å. (1987). Chemical abundances in molecular clouds. In Interstellar Processes, D. J. Hollenbach & H. A. Thronson, Jr., eds., (D. Reidel: Dordrecht), p 561

Irvine, W. (1996). Personal Communication.

Lacy, J.H., Baas, F., Allamandola, L.J., Persson, S.E., McGregor, P.J., Lonsdale, C.J., Geballe, T.R., & van der Bult, C.E.P. (1984). 4.6 micron absorption features due to solid phase CO and cyano group molecules toward compact infrared sources. *ApJ* **276**, 533.

Mann, A. P. C., & Williams, D. A. (1980). A list of interstellar molecules. *Nature*, **283**, 721.

Moore, M. H., Ferrante, R. F., & Nuth, J. A. (1996). Infrared spectra of proton irradiated ices containing methanol. *Planet. Spa. Sci.*, **44**, 927.

Nuth, J. A., and Moore, M. H. (1988). SiH and the unidentified 4.6 micron feature. *ApJ*, **329**, L113.

Russo, N. D., and Khanna, R. K. (1996). Laboratory Infrared Spectroscopic Studies of Crystalline Nitriles with Relevance to Outer Planetary Systems. *Icarus*, **123**, 366.

Sandford, S.A. (1996). The Inventroy of Interstellar materials available for the formation of a Solar System. *Meteoritics and Planetary Science* **31**, 449.

Sandford, S.A., & Allamandola, L.J. (1993). Condensation and Vaporization Studies of CH_3OH and NH_3 Ices: Major Implications for Astrochemistry. *ApJ* **417**, 815.

Sandford, S.A., Allamandola, L.J., Tielens, A.G.G.M., & Valero, G.J. (1988). Laboratory Studies of the Infrared Spectral Properties of CO in Astrophysical Ices. *ApJ* **329**, 498.

Schutte, W.A., Allamandola, L.J., & Sandford, S.A. (1993a). Formaldehyde and organic molecule production in astrophysical ices at cryogenic temperatures. *Science* **259**, 1143.

Schutte, W. A., Allamandola, L. J., & Sandford, S. A. (1993b). Organic Molecule Production in Cometary Nuclei and Interstellar Ices by Thermal Formaldehyde Reactions. *Icarus* **104**, 118.

Tegler, S.C., Weintraub, D.A., Allamandola, L.J., Sandford, S.A., Rettig, T.W., & Campins, H. (1993). Detection of the 2165 cm⁻¹ (4.619 µm) XCN Band in the Spectrum of L1551 IRS 5. *ApJ* **411**, 260.

Tegler, S.C., Weintraub, D.A., Rettig, T.W., Pendleton, Y.J., Whittet, D.C.B., & Kulesa, C.A. (1995). Evidence for chemical processing of precometary icy grains in circumstellar environments of pre-main-sequence stars. *ApJ* **439**, 279.

Tielens, A.G.G.M., & Hagen, W. (1982). Model calculations of the molecular composition of interstellar grain mantles. *A&A* **114**, 245.

Tielens, A.G.G.M., Tokunaga, A.T., Geballe, T.R., & Baas, F. (1991). Interstellar solid CO: Polar and nonpolar interstellar ices. *ApJ* **381**, 181.

van Dishoeck, E.F., Blake, G.A., Draine, B.T., & Lunine, J.I. (1993). The Chemical Evolution of Protostellar and Protoplanetary Matter. In *Protostars and Planets III*, eds. E. Levy & J. Lunine, (Univ. of Arizona Press: Tucson), p. 163.

Willner, S.P., Gillett, F.C., Herter, T.L., Jones, B., Krassner, J., Merrill, K.M., Pipher, J.L., Puetter, R.C., Rudy, R.J., Russell, R.W., & Soifer, B.T. (1982). Infrared spectra of protostars: Composition of the dust shells. *ApJ*, **253**, 174.

Wolman, Y., Miller, S.L., Ibanez, J., & Oro, J. (1971). Formaldehyde and ammonia as precursors to prebiotic amino acids. *Science*, **174**, 1039.